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Research paper

Polymeric hybrid iodoplumbates and iodobismuthates containing mono- and bisalkylated derivatives of 1,2-bis(4-pyridyl)ethylene: Structural and optical features

Andrey N. Usoltsev [a], Sergey A. Adonin [a,b,*], Pavel A. Abramov [a,b], Ilya V. Korolkov [a,b], Irina V. Yushina [a], Olga V. Antonova [a], Maxim N. Sokolov [a,c], Vladimir P. Fedin [a,b]

[a] Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Lavrentiev Ave. 3, Novosibirsk, Russia
[b] Novosibirsk State University, 630090, Pirogova St. 2, Novosibirsk, Russia
[c] Kazan Federal University, Alexander Butlerov Institute of Chemistry, Lobachevskogo Str. 1/29, 420008 Kazan, Russia

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ABSTRACT

Reactions of PbI_2 with *N*-alkylated derivatives of 1,2-bis(4-pyridyl)ethylene (bpen) MeBpenI and Me_2BpenI_2 result in 1D-polymeric complexes [{Pb(MeBpen)I_3}] (**1**) and (Me_2bpen)[{PbI_3}]$_2$ (**2**). For both compounds, band gap values were determinated experimentally; **1** demonstrates weak red luminescence. Binuclear hybrid iodobismuthate [Bi_2(MeBpen)$_2I_8$] (**3**) was obtained by the similar scheme using BiI_3 instead of PbI_2.

1. Introduction

Over the last years, halide, in particular iodide complexes of late transition and post-transition metals attract an ongoing attention of inorganic chemists [1–7]. Apart of the fundamental aspects of this area, this interest is inspired by numerous physical and chemical properties, including catalysis [5–8], thermochromism [4,9–13], ferroelectricity etc. [14–22] An urgent and fast-growing field of application for iodometalates is design of solar cells based thereupon. The lion's share of present research is concentrated on iodoplumbates which reveal the best characteristics (PCE up to 21%) [23–27], but there are also numerous attempts to involve other metal iodides: Bi(III) [28–30], Ge(II) [31], Sb(III) [32] etc. It must be noted that although this area is developing very rapidly, the number of compounds tested in photovoltaics is still rather limited. Generally, this fact can be explained by the dominant paradigm proposing the use of cations, such as Cs^+ or methylammonium, which yield in good characteristics for iodoplumbates, but it does not guarantee desired results in the case of other metals. Therefore, the studies of new iodometalates, including various organic-inorganic hybrids, as well as establishment of their optical properties, are needed for further progress in this field. In this work, we report three novel iodide complexes of Pb(II) and Bi(III) based on mono- and bis-methylated 1,2-bis(4-pyridyl)ethylene (bpen), their crystal structures and optical properties (band gaps), as well as luminescence.

2. Experimental section

All reagents were obtained from commercial sources and used as purchased. Iodides of mono- and bis-methylated bpen (MeBpenI and Me_2BpenI_2) were obtained by reactions of bpen with one or two equivalents of CH_3I and identified by ^{1}H NMR spectra and CHN composition. IR spectra were recorded on Scimitar FTS 2000 spectrometer.

2.1. Synthesis of [{Pb(MeBpen)I_3}] (**1**)

100 mg (0.22 mmol) of PbI_2 and 70 mg (0.22 mmol) of MeBpenI were dissolved in 10 ml of DMF, kept for 50 min at 100 °C and then cooled down. Dark red crystals of **1** were obtained by slow

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Lavrentiev Ave. 3, Novosibirsk, Russia.
E-mail address: adonin@niic.nsc.ru (S.A. Adonin).

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